

SULFUR ISOTOPIC STUDIES OF ARCHEAN SLATE AND GRAYWACKE  
FROM NORTHERN MINNESOTA: EVIDENCE FOR THE EXISTENCE  
OF SULFATE REDUCING BACTERIA

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## ABSTRACT

Sulfur isotopic studies of pyrite from metasediments in the >2.6 b.y. old Deer Lake greenstone sequence, Minnesota, have been conducted in order to evaluate the possible importance of sulfate reducing bacteria in sulfide formation. Pyrite occurs as ovules up to 2 cm. in diameter within graphitic slates, and as fine disseminations in metagraywacke units. SEM studies indicate the pyrite is framboidal in morphology.

$\delta^{34}\text{S}$  values of pyrite from the Deer Lake sediments range from -2.3 to 11.1 o/oo, with a peak at  $\sim +2$  o/oo. Isotopic data is consistent with either high temperature inorganic reduction of circulating seawater sulfate, or low temperature bacterial reduction. However, the lack of sulfide bands or massive occurrences in the sediments, the restriction of pyrite mineralization to the sediments, and the absence of evidence for hot spring activity suggest that a diagenetic origin of pyrite is more feasible. Sulfide in such an environment would be produced principally by the action of sulfate reducing bacteria.

Results of the study are in agreement with those of Goodwin et al. (Econ. Geol., 1976) who suggest that dissimilatory sulfate reduction was operative in the Archean ocean some 2.75 b.y. ago.

## INTRODUCTION

The Deer Lake greenstone sequence is located in north-central Minnesota, about 100 km north of Duluth (Figure 1). Rock types are similar to those found in other Archean greenstone belts and consist of layered sills, ultramafic lenses, mafic-intermediate flows, and sedimentary material. Metamorphism is of the greenschist facies. The sequence is cut by a gabbroic dike swarm dated at 2.0-2.2 b.y. (Hanson and Malhotra, 1971), and is thought to be correlative with the >2.6 b.y. old greenstone sequences located to the east within the well-known Vermillion District (Sims, 1972).

The bulk of the rocks in the area are volcanic or shallow sub-volcanic in nature (Figure 2). Prospecting for Cu-Ni ore deposits occurred in the late nineteen-sixties and early seventies, largely because of the environmental similarities to Ni-sulfide occurrences in Canada and Australia. Although results of exploration were in general negative, large amounts of drill core from the evaluation provided access to the study of a major portion of the volcano-sedimentary sequence.

This paper deals primarily with an investigation of a series of metasedimentary units discovered as a result of the drilling program. Sediments consist of graywackes and highly graphitic slates and argillites. Of particular interest was the relatively

large amount of pyrite (up to 10 volume percent) found in the metasediments. Pyrite in the carbonaceous units bears a strong similarity to pyrite found in more recent black shale and coal deposits. Production of sulfide in these occurrences is generally attributed to action of sulfate-reducing bacteria. In order to gain some insight into the possible presence and origin of sulfate reducing bacteria in Archean time a sulfur isotopic study of the pyrite-bearing metasediments was initiated. Similar studies of sediments from the 3.7 b.y. old Isua, West Greenland, sequence by Monster et al. (1979) indicate that sulfate reducing bacteria were not active during this time period. Goodwin et al. (1976) suggest that sulfate reducing bacteria played a major role in the formation of pyrite found in the Michipicoten and Woman River iron-formations (2.75 b.y.) in Canada.

#### LOCAL GEOLOGY

Igneous rocks of the Deer Lake sequence have been studied by Berkley and Himmelberg (1978) and Ripley (1978, 1979). The bulk of the igneous rocks comprise what is known as the Deer Lake Complex (Berkley and Himmelberg, 1978), which consists of two layered peridotite-pyroxenite-gabbro sills, a gabbroic body whose basal section is not exposed, and two ultramafic lenses. At least eight mafic and intermediate, mostly pillowed, lava flows occur in the area with a combined thickness of



~180 m (Ripley, 1973). The flows are intercalated with the metasedimentary rocks. Graywackes occur in sequences never more than 10 m in thickness. They contain abundant volcanic detritus and are thought to be in part derived from the underlying volcanics. Slate units are strongly associated with graywacke, and may reach thicknesses of up to 15 m. Drill core data indicate that rocks of the Deer Lake Complex occur stratigraphically below the flows and metasediments (Figure 2).

The entire Deer Lake sequence is flanked by plutonic rocks, the Effie Pluton to the north and the Zeisser's Island Pluton to the south (Figure 1).

Metamorphism in the area has preserved primary textures but altered mineralogies. Olivine is extensively serpentinized, pyroxene is altered to amphibole, and plagioclase has been saussuritized (chlorite, epidote, calcite, zoisite).

## TEXTURE, MORPHOLOGY, AND DISTRIBUTION OF PYRITE IN THE META- SEDIMENTARY ROCKS

Within the graphitic slates pyrite occurs as ovules ranging from less than 1 mm to 2 cm in diameter (Figure 3). Although several ovules may occur in close proximity the sulfide mineralization is never massive in nature. Several ovules were extracted for scanning electron microscope examination following methods outlined by Neuerberg (1961, 1975). At all magnifications (up to 2,000 X) pyrite displayed a framboidal form. Such morphology is common in pyrite produced during diagenesis of carbonaceous sediments, although framboidal pyrite is not restricted to such environments.

Pyrite in the graywacke units is more finely disseminated, with grain size seldom in excess of one mm. Sulfide concentrations are never as high as those in the slates, with pyrite averaging about one volume percent.

Sulfide minerals are generally uniformly distributed horizontally and vertically within the sulfide-bearing meta-sediments. Although rare, clusters of ovules are locally found within a particular lateral horizon. Concentrations of pyrite along fractures occurs uncommonly, and is attributed to remobilization of primary pyrite. Mineralization normally has little relationship with joint or fracture systems.

## SULFUR ISOTOPIC STUDY

*Analytical Methods*

Fifty-two samples of pyrite from the Deer Lake sediments were analyzed for sulfur isotopic composition. Coarse pyrite ovules were drilled with a dental drill and the resulting powder burned in vacuum with an excess of CuO to produce SO<sub>2</sub> for isotopic analysis. Samples containing fine-grained sulfides were acid-digested with residual solutions checked for sulfate production and treated with a mixture of HI-H<sub>3</sub>PO<sub>2</sub>-HCl (Thode et al., 1961). The resulting H<sub>2</sub>S was first converted to CdS and then to Ag<sub>2</sub>S that was burned as described above.

Analyses were performed utilizing a modified 6", 60° sector isotope ratio mass spectrometer. Results are expressed in "delta notation" where

$$\delta^{34}\text{S} (\text{o/oo}) = \left[ \frac{\frac{34\text{S}}{32\text{S}} \text{ sample}}{\frac{34\text{S}}{32\text{S}} \text{ standard}} - 1 \right] \times 1000$$

with Canyon Diablo Troilite as the standard. Sample reproducibility was generally within 0.3 o/oo.

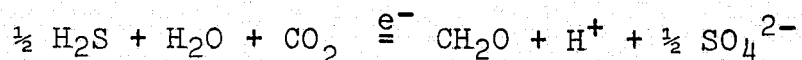
### Results

$\delta^{34}\text{S}$  values of pyrite from the Deer Lake sediments are displayed in Figure 4 and tabulated in Table 1. Values range from -2.3 to +11.1 o/oo. As shown in Table 1  $\delta^{34}\text{S}$  values vary erratically over short distances of drill core. Fluctuations as large as 5 o/oo may occur within a vertical distance of ~3m. There are no easily identifiable vertical or horizontal trends, although correlations between drill holes is virtually impossible due to structural complexities. It is interesting to note that  $\delta^{34}\text{S}$  values from drill hole 26515 are consistently above 4 o/oo. This section is the westernmost of the study area and suggests that some type of isotopic zoning may be present. Unfortunately the lack of outcrop or drill core information from areas farther to the west hampers further investigation of this possibility.

Affects of greenschist metamorphism on the sulfur isotope ratios are thought to be negligible. Although metamorphism may alter the sulfur isotopic distribution between coexisting phases, the overall sulfur isotopic composition of a particular horizon is generally preserved (see Ripley and Ohmoto, 1977; Rye and Ohmoto, 1974). The presence of only pyrite in the Deer Lake sediments reduces the possibility of any large scale redistribution of  $\delta^{34}\text{S}$  values due to metamorphism.

## DISCUSSION

Before proceeding with an evaluation of possible origins of sulfide in the Deer Lake sediments, a point must be made regarding the presence of sulfate in Archean seawater. The occurrence of barite in rocks of The Fig Tree Group, South Africa (Heinrichs and Reimer, 1977) indicates that at least minor quantities of sulfate were present in Archean seawater. Broda (1975) has proposed that green and purple sulfur oxidizing bacteria (photolithotrophic bacteria) supplied sulfate to seawater by reactions similar to:



In addition some sulfate would certainly have been available from volcanic activity. Although limited in scope, current evidence suggests that sulfate may have been plentiful in the oceanic environment during Archean times (and probably before the attainment of free oxygen in the contemporaneous atmosphere).

### *Sulfide Genesis in the Metasedimentary Rocks*

In order to evaluate the origin of sulfide found in pyrite of the Deer Lake sediments several alternative models must be considered. Geologic and isotopic data, taken together, serve

to restrict the number of feasible alternatives. Several possible models for pyrite generation are listed below, followed by a discussion of their relative merit.

- A) Sulfide derived from primary volcanic fluids issuing as hot springs in the sedimentary basin.
- B) Sulfate in circulating seawater reduced to sulfide at high temperatures ( $>250^{\circ}\text{C}$ ), and sulfide mineral deposition again the result of hot spring emanations.
- C) Sulfide produced by either methods A or B and transported into the basin after issuing from a vent area outside the depositional basin.
- D) Sulfide produced from sulfate within the basin by the action of sulfate reducing bacteria.

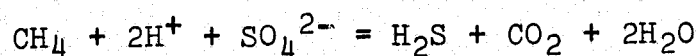
Sulfide mineralization due to hot spring activity has been suggested for several stratiform sulfide ore occurrences (e.g. Ohmoto and Rye, 1979; Bachinski, 1977; Ripley and Ohmoto, 1977; Solomon et al., 1969). Sulfur may be of either primary magmatic origin or can be produced by inorganic reduction of sulfate in convectively circulating seawater. However, hot spring activity within the Deer Lake area is not well supported by geological evidence. Feeder pipes or mineralized fracture zones have not been found. The lack of massive iron sulfide horizons and the restriction of pyrite to ovules or fine disseminations within the sediments suggests that direct hot spring emanations were not

important. For these reasons models A and B are considered unlikely mechanisms for sulfide production and pyrite genesis in the Deer Lake sequence.

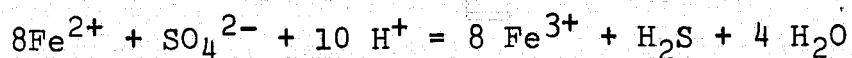
Model C must be evaluated from the standpoints of sulfide derivation from volcanic and seawater sources. Isotopic data strongly suggests that primary igneous sulfur ( $\delta^{34}\text{S} \sim 0$  o/oo) could not have been the source of  $\text{H}_2\text{S}$  from which pyrite formed. Ohmoto (1972) has shown that small fluctuations in physicochemical parameters ( $f\text{O}_2$ , pH, T, etc.) can cause isotopic variations similar to those found in the Deer Lake sediments. Variations in  $\delta^{34}\text{S}$  values are greatest where nearly equal amounts of oxidized sulfur and reduced sulfur species are in isotopic equilibrium. However,  $\delta^{34}\text{S}$  values as high as +4 o/oo cannot be produced in the pyrite stability field from a fluid having a source  $\delta^{34}\text{S}$  near 0 o/oo (see for example Ohmoto and Rye, 1979). Isotopic evidence indicates that if hydrothermal deposition occurred, the source of sulfide found within pyrite was certainly characterized by a  $\delta^{34}\text{S}$  value greater than  $\sim +6$  o/oo, and probably greater than +12 o/oo if the +11.1 value of one pyrite sample from a slate unit is considered (Figure 4).

Reduction of seawater sulfate appears to be the most feasible method capable of producing the observed range in pyrite  $\delta^{34}\text{S}$  values. The principal question is whether this

reduction was biologic or abiologic in nature. Introduction of externally derived fluids to the basin is difficult to refute. Circulating seawater may have leached iron from country rocks, contained sulfate may have been reduced to sulfide, and both sulfur and metals transported to the basin and deposited there as pyrite. Sulfate may have been inorganically reduced to sulfide at high temperatures by reaction with carbonaceous material or ferrous iron contained in the volcanics. For example methane may have been abundant in environments favorable for black shale accumulation. Sulfate may have been reduced via a reaction similar to:



Reduction of sulfate by ferrous iron may have proceeded according to a reaction similar to (Ohmoto and Rye, 1979; Ripley and Ohmoto, 1977):



$\delta^{34}\text{S}$  values of  $\text{H}_2\text{S}$  produced by such reactions are a function of several physicochemical parameters (see above), all in essence reflecting the degree of reduction of a given mass of sulfate to sulfide. Total conversion would result in  $\delta^{34}\text{S}_{\text{H}_2\text{S}} = \delta^{34}\text{S}_{\text{SO}_4^{2-}}$ . Partial reduction would result in  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  values lower than the source sulfate value. Figure 5 illustrates the expected variations from inorganic reduction of seawater sulfate (see Ohmoto and Rye, 1979). Although some  $\text{H}_2\text{S}$  contained in a hydrothermal fluid



being transported within  $\text{SO}_4^{2-}$ -rich waters may re-oxidize to sulfate, very little isotopic fractionation would be expected due to kinetic isotope effects.

The range in  $\delta^{34}\text{S}_{\text{pyrite}}$  values found in the Deer Lake area can be accounted for by distal inorganic reduction of seawater sulfate, followed by transport and deposition in the accumulating sedimentary sequence. However, geologic evidence again suggests that such a process was unlikely. Deposition from hydrothermal fluids would be relatively rapid and would be expected to produce sulfidic bands and, at least locally, massive sulfide zones. Such features are totally absent in the Deer Lake sediments.

A diagenetic model for pyrite, with sulfide produced by bacterial reduction of seawater sulfate is consistent with geologic and isotopic data. In such a process seawater sulfate is bacterially reduced to hydrogen sulfide and through reactions with detrital iron minerals in the sediments iron sulfides form (Berner, 1970). The occurrence of framboidal pyrite ovules, although not conclusive evidence, is highly suggestive of diagenetic pyrite. According to Sweeney and Kaplan (1973) diagenetic pyrite may form as either single crystals (as common in the graywackes) or framboids.

Schwarcz and Burnie (1973) and Ohmoto and Rye (1979) have reviewed occurrences of bacterially reduced sulfide in sedimentary

rocks. Figure 5 illustrates the expected range in  $\delta^{34}\text{S}$  values for sedimentary sulfide produced in systems open to sulfate (rate of sulfate supply is greater than the rate of reduction) and closed to sulfate (rate of reduction is faster than the rate of sulfate supply). The  $\delta^{34}\text{S}_{\text{pyrite}}$  values observed in the Deer Lake sequence are clearly similar to those expected from closed system bacterial reduction. Such a system may be further divided on the basis of availability of metal which may combine with produced  $\text{H}_2\text{S}$  (or  $\text{HS}^-$ ). Following the reasoning of Ohmoto and Rye (1979) a system closed to  $\text{H}_2\text{S}$  is one where the supply of iron is insufficient to utilize all the aqueous sulfide as iron sulfide. A system open to  $\text{H}_2\text{S}$  is one where all produced aqueous sulfide is consumed in the formation of iron sulfide.

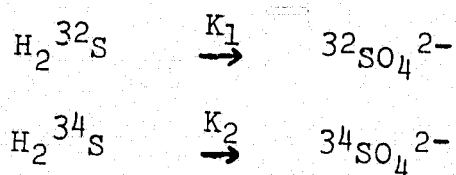
Assuming that most reduction takes place at the sediment-water interface and occurs without vertical diffusion a Rayleigh process may be used to trace the  $\delta^{34}\text{S}$  values of  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  (Jorgensen, 1979; Ohmoto and Rye, 1979; Goldhaber and Kaplan, 1974). The isotopic composition of sulfate at any time  $t$  may be computed as follows:

$$\delta^{34}\text{S}_{\text{SO}_4^{2-}(t)} = \delta^{34}\text{S}_{\text{SO}_4^{2-}(o)} + 1000 \left( f^{1-\frac{K_1}{K_2}} - 1 \right)$$

where  $\delta^{34}\text{S}_{\text{SO}_4^{2-}(o)} = \delta^{34}\text{S}_{\text{SO}_4^{2-}}$  original

$f$  = fraction of  $\text{SO}_4^{2-}$  remaining

$\frac{K_1}{K_2}$  = kinetic isotope effect defined as the ratio of rate constants for the reactions:



In order to utilize the Rayleigh model the  $\delta^{34}\text{S}$  value of Archean seawater sulfate ( $\delta^{34}\text{S}_{(o)}$ ) must be known, along with  $K_1/K_2$ . Because of the scarcity of Archean evaporites the  $\delta^{34}\text{S}$  value of Archean seawater sulfate is difficult to estimate. Schwarcz and Burnie (1973) suggest that it probably did not vary outside the range of  $\delta^{34}\text{S}$  values for Phanerozoic seawater sulfate (+10 - +30 o/oo). In order to test the consistency of the model a value of +14 o/oo has been assumed for  $\delta^{34}\text{S}_{\text{SO}_4^{2-}(o)}$ . Utilizing the peak  $\delta^{34}\text{S}_{\text{pyrite}}$  value (+2 o/oo, Figure 4) and the assumed  $\delta^{34}\text{S}$  value for seawater sulfate ( $\Delta_{\text{SO}_4^{2-} - \text{H}_2\text{S}} = 12$  o/oo) a  $K_1/K_2$  value of 1.012 is derived (see Schwarcz and Burnie, 1973). This value is consistent with experimentally measured sulfate-

sulfide fractionation for bacterial reduction (e.g. Harrison and Thode, 1958).

Results of the calculations are presented in Table 2.  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  values have been computed assuming that the system is initially open to aqueous sulfide (sufficient iron to precipitate iron sulfide), and therefore  $\Delta_{\text{SO}_4^{2-} - \text{H}_2\text{S}}$  remains constant. Note that at about 50 percent reduction there is a cutoff in observed  $\delta^{34}\text{S}_{\text{pyrite}}$  values. This is interpreted as indicating a limited abundance of metal; in other words only the first 50 percent of produced sulfide was able to react with iron to form pyrite.

It must be emphasized that the Rayleigh model is presented here only as an illustration of principles. Because of the assumptions mentioned above it cannot quantitatively model the proposed reduction process. The Rayleigh model predicts a continual increase in  $\delta^{34}\text{S}$  values that would be manifested in a trend of heavier pyrite  $\delta^{34}\text{S}$  values upward in the stratigraphic sequence. No trends of this type have been observed in the Deer Lake sediments. The inference is that although the range in pyrite  $\delta^{34}\text{S}$  values may be in part explained by a Rayleigh model, the reduction was more complicated than a single batch process. Periodic influxes of fresh sulfate, variations in the rate of sulfate reduction, reduction below the sediment-water interface, and possible vertical diffusion of sulfate and sulfide

(Jorgensen, 1979) are some of the factors that may have complicated the process.

In summary the sulfur isotopic data strongly suggest that sulfide found in pyrite of the Deer Lake sediments was produced by reduction of sulfate having a  $\delta^{34}\text{S}$  value greater than  $\sim 12$  o/oo. Geologic and isotopic evidence are consistent with a diagenetic model of pyrite formation, with sulfide produced due to the activity of sulfate-reducing bacteria. The somewhat restricted range in pyrite  $\delta^{34}\text{S}$  values may be due to cessation of iron sulfide precipitation caused by an insufficient supply of iron.

#### *Environment of Pyrite Deposition*

Closed system bacterial reduction has generally been interpreted as indicating shallow, brackish water conditions (e.g. Ohmoto and Rye, 1979; Schwarcz and Burnie, 1973). In the Deer Lake area the presence of well developed pillowed metabasalts and the sedimentary sequence shale-graywacke cast doubt on the applicability of shallow water conditions. However, although comparisons with modern systems may not be justified, present day marine basins (particular along certain continental margins) with restricted circulation are well known (Grosline, 1978). A deep basin with restricted circulation of seawater would behave as a closed system in terms of bacterial reduction of seawater sulfate at or near the sediment-seawater interface.

As mentioned above the reduction may also occur below this interface, and therefore essentially be isolated from the sulfate reservoir.

Slates and graywackes from the Onwatin Formation in Sudbury, Ontario (Thomson, 1956) have  $\delta^{34}\text{S}$  values similar to those of the Deer Lake sediments. Schwarcz and Burnie (1973) have proposed the existence of a deep marine basin with restricted circulation to account for the apparent contradiction between lithologies indicative of deep water conditions and isotopic values indicative of closed system conditions. Additional work is needed to clarify the sulfur isotope systematics in slate-graywackes sequences similar to those at Deer Lake and Sudbury.

#### *Implications for the Appearance of Sulfate Reducing Bacteria*

Geologic and isotopic data collected from the Deer Lake sediments are supportive of sulfide formation due principally to the action of sulfate reducing bacteria. With the advent of more precise dating techniques perhaps the age of the Deer Lake and Vermilion greenstone sequences will be better defined. Until then all that can be said is that sulfate reducing bacteria were apparently active in the Archean at ~2.6-2.7 b.y. This is in strong agreement with Goodwin et al. (1976) who have proposed

the presence of sulfate reducers at ~2.75 b.y. In light of the evidence against the existence of sulfate reducing bacteria in Isuan time (3.7 b.y., Monster et al., 1979) further studies to precisely bracket the time of evolution of dissimilatory sulfate reduction should focus on the time interval 2.7-3.7 b.y.

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## REFERENCES

- Bachinski D. J. (1977) Sulfur isotopic composition of ophiolitic cupriferous iron sulfide deposits, Notre Dame Bay, Newfoundland. Econ. Geol. 72, 243-258.
- Berkley J. L. and Himmelberg, G. R. (1978) Cumulus mineralogy and petrology of the Deer Lake Complex, Itasca County, Minnesota. Minn. Geol. Survey Report of Inv. 20A.
- Berner R. A. (1970) Sedimentary pyrite formation. Am. J. Sci. 268, 1-23.
- Broda E. (1975) *The Evolution of the Bioenergetic Processes.* Pergamon Press.
- Goldhaber M. B. and Kaplan I. R. (1974) The sulfur cycle. In *The Sea, Vol. 5, Marine Chemistry* (ed. E. D. Goldberg), pp. 569-655. Wiley.
- Goodwin, A., Monster, J. and Thode H. G. (1976) Carbon and sulfur isotope abundances in Archaean iron-formations and Early Precambrian life. Econ. Geol. 71, 870-891.
- Gorsline D. S. (1978) Anatomy of margin basins. Jour. Sed. Pet. 48, 1055-1068.
- Hanson G. N. and Malhotra R. (1971) K-Ar ages of mafic dikes and evidence for low-grade metamorphism in northeastern Minnesota. Geol. Soc. Amer. Bull. 82, 1107-1113.

- Harrison A. G. and Thode H. G. (1958) Mechanism of the bacterial reduction of sulfate from isotope fractionation studies. Faraday Soc. Trans. 54, 84-92.
- Heinrichs T. K. and Reimer T. O. (1977) A sedimentary barite deposit from the Archean Fig Tree Group of the Barberton Mountain Land (South Africa). Econ. Geol. 72, 1426-1441.
- Jørgensen B. B. (1979) A theoretical model of the stable sulfur isotope distribution in marine sediments. Geochim. Cosmochim. Acta 43, 363-374.
- Monster J., Appel P. W. U., Thode H. G., Schidlowski M., Carmichael C. M. and Bridgwater D. (1979) Sulfur isotope studies in early Archaean sediments from Isua, West Greenland: implications for the antiquity of bacterial reduction. Geochim. Cosmochim. Acta 43, 405-413.
- Neuerberg G. J. (1961) A method of mineral separation using hydrofluoric acid. Am. Min. 46, 1498-1501.
- Neuerberg G. J. (1975) A procedure using hydrofluoric acid for quantitative mineral separation from silicate rocks. U.S.G.S. Jour. Res. 3, 377-378.
- Ohmoto H. (1972) Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. Econ. Geol. 67, 551-578.
- Ohmoto H. and Rye R. O. (1979) Isotopes of sulfur and carbon. In *Geochemistry of Hydrothermal Ore Deposits* (ed. H. L. Barnes), pp. 509-567. Wiley-Interscience.

- Ripley E. M. (1973) The ore petrology and structural geology of the Deer Lake mafic-ultramafic complex, Effie, Itasca County, Minnesota. Unpubl. M.S. thesis, Univ. of Minn., Duluth.
- Ripley E. M. and Ohmoto H. (1977) Mineralogic, sulfur isotope, and fluid inclusion studies of the stratabound copper deposits at the Raul mine, Peru, South America. Econ. Geol. 72, 1017-1041.
- Ripley E. M. (1978) Sulfides in the layered sills of the Deer Lake Complex, Minnesota. Minn. Geol. Survey Report of Inv. 20B.
- Ripley E. M. (1979) Sulfide petrology of basal chilled margins in layered sills of the Archean Deer Lake Complex, Minnesota. Contrib. Mineral. Petrol. 69, 345-354.
- Rye R. O. and Ohmoto H. (1974) Sulfur and carbon isotopes and ore genesis: a review. Econ. Geol. 69, 824-843.
- Schwarcz H. P. and Burnie S. W. (1973) Influence of sedimentary environment on sulfur isotope ratios in clastic rocks: a review. Mineral. Deposita 8, 264-277.
- Sims P. K. (1970) Geologic map of Minnesota. Minn. Geol. Survey Misc. Map Series, Map M-14.
- Sims P. K. (1972) Northern Minnesota, general geologic features. In *Geology of Minnesota: A Centennial Volume* (eds. P. K. Sims and G. B. Morey), pp. 41-49. Minn. Geol. Survey.

- Solomon M., Rafter T. A. and Jensen M. L. (1969) Isotope studies on the Roseberg, Mt. Farrell, and Mount Lyell ores, Tasmania. Mineral. Deposita 4, 172-199.
- Sweeney R. E. and Kaplan I. R. (1973) Pyrite framboid formation: laboratory synthesis and marine sediments. Econ. Geol. 68, 618-635.
- Thode H. G., Monster J. and Dunford H. B. (1961) Sulfur isotope geochemistry. Geochim. Cosmochim. Acta 25, 159-174.
- Thomson J. E. (1956) Geology of the Sudbury Basin. Ontario Dept. Mines Ann. Rep. 65, 1-56.

## FIGURE CAPTIONS

- Figure 1. Regional geologic map of northeastern Minnesota, showing location of the Deer Lake greenstone sequence. Taken from the Geologic Map of Minnesota (Sims, 1970).
- Figure 2. Generalized stratigraphy in the Deer Lake area.
- Figure 3. Pyrite ovules in graphitic slate from the Deer Lake sequence. The core is 6 cm long and 4 cm wide.
- Figure 4.  $\delta^{34}\text{S}$  values of pyrite from sediments in the Deer Lake volcano-sedimentary sequence.
- Figure 5. Theoretical distribution of  $\delta^{34}\text{S}$  values of  $\text{H}_2\text{S}$  and sulfide minerals produced by reduction of seawater sulfate. Modified from Ohmoto and Rye (1979).

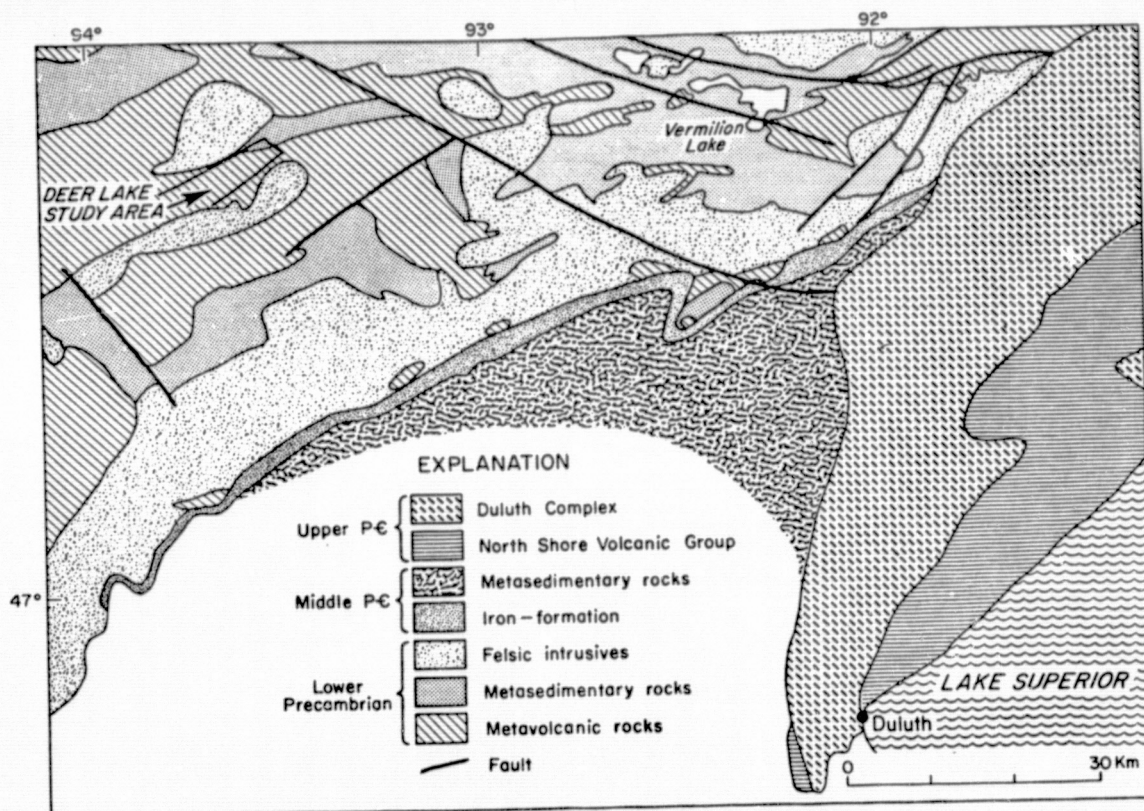
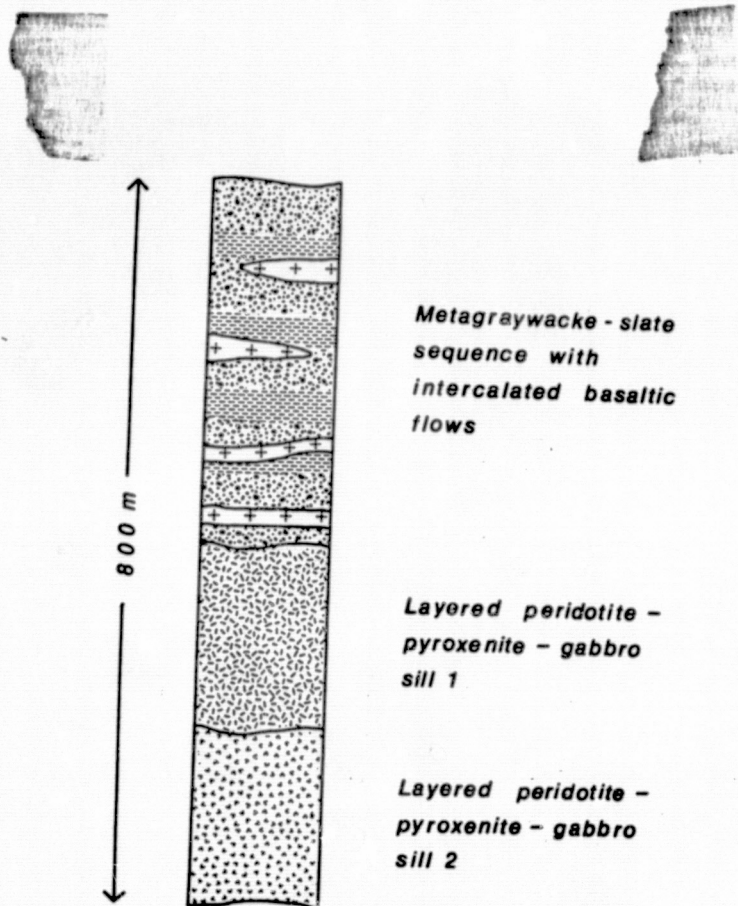


Fig. 1





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Fig. 2



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Figure 3



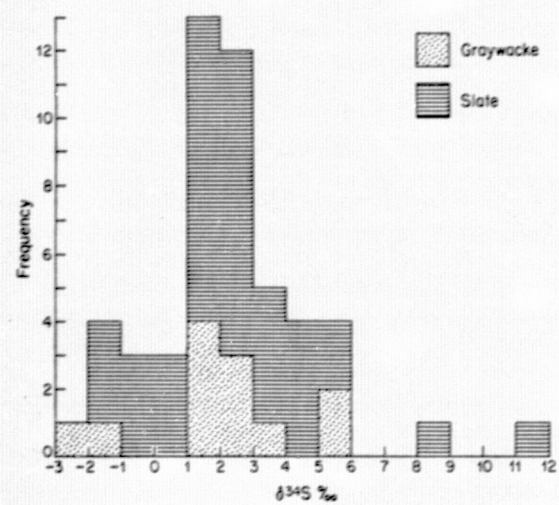


Fig. 4

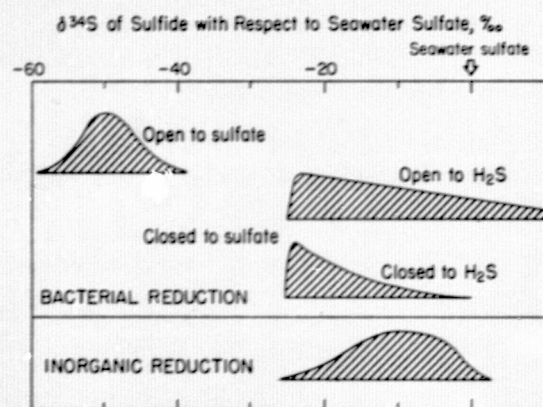


Table 1. Sulfur isotopic composition of pyrite in slate and graywacke from the Deer Lake volcano-sedimentary sequence.

Depth, meters	Rock Type	$\delta^{34}\text{S}$ , o/oo
<u>Drill Hole 26052</u>		
127.4	slate	1.5
127.6	"	1.3
151.5	"	1.1
152.0	"	2.7
152.1	"	3.3
152.4	"	3.6
152.6	"	1.7
152.7	"	4.7
152.9	"	2.9
153.0	"	2.6
157.4	"	3.1
157.6	"	2.9
157.9	"	2.9
158.2	"	2.6
158.5	"	3.3
<u>Drill Hole 26503</u>		
279.8	slate	1.1
299.4	"	1.2
299.7	"	-1.4
299.8	"	0.3
300.3	"	-0.5
300.4	"	-0.3
310.6	"	0.3
311.5	graywacke	1.4
313.2	"	3.7
313.3	slate	0.9
314.2	"	-1.4
315.1	"	-1.3
345.5	graywacke	1.7
345.7	slate	-0.5
346.1	graywacke	1.8
346.4	"	-1.4
<u>Drill Hole 26506</u>		
96.7	slate	2.7
97.6	"	1.8
99.1	"	2.7
106.8	graywacke	1.7
122.6	"	5.1

Table 1 (cont'd.)

Drill Hole 26508

121.5	slate	2.4
121.7	graywacke	3.0
136.4	"	2.6
140.6	"	2.9
141.5	slate	1.7
146.4	"	1.1

Drill Hole 26509

93.9	slate	11.1
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Drill Hole 26515

119.1	graywacke	6.0
119.4	slate	4.4
119.7	"	8.0
127.9	"	4.3
128.0	"	5.3
128.2	"	4.6
128.3	"	5.2

Drill Hole 26516

99.8	slate	1.5
126.1	graywacke	-2.4

Table 2. Results of calculations utilizing the Rayleigh equation for closed system bacterial reduction

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$$\delta^{34}\text{S}_{\text{SO}_4^{2-}(\text{t})} = \delta^{34}\text{S}_{\text{SO}_4^{2-}(\text{o})} + 1000 \left( f^{1-\frac{K_1}{K_2}} - 1 \right)$$

$$\delta^{34}\text{S}_{\text{SO}_4^{2-}(\text{o})} = + 14 \text{ o/oo} \quad K_1/K_2 = 1.012$$


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<u>f</u>	<u><math>\delta^{34}\text{S}_{\text{SO}_4^{2-}(\text{t})}</math></u>	<u><math>\delta^{34}\text{S}_{\text{H}_2\text{S}(\text{t})}</math></u>
1	14.0	2.0
.9	15.3	3.3
.8	16.7	4.7
.7	18.3	6.3
.6	20.1	8.1
.5	22.3	10.3
.4	25.1	cut-off in observed values

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